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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE Spring 1996 (April)		3. REPORT TYPE AND DATES COVERED Final Report
4. TITLE AND SUBTITLE NATIVE-OXIDE-DEFINED SEMICONDUCTOR QUANTUM WELL LASERS AND OPTOELECTRONIC DEVICES: Al-BASED III-V NATIVE OXIDES			5. FUNDING NUMBERS  DAAH03-92-G-0264	
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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  University of Illinois Department of Electrical and Computer Engineering 155 Everitt Laboratory 1406 W. Green St., Urbana, IL 61801-2991			10. SPONSORING/MONITORING AGENCY REPORT NUMBER  ARO 30090.26-EL	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)  U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211			11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.	
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  At atmospheric conditions high Al composition $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ( $x \geq 0.7$ ) in $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$ heterostructures is subject to failure via hydrolyzation. In contrast, "wet" oxidation at higher temperatures ( $\geq 400^\circ\text{C}$ ) produces stable AlGaAs native oxides (Urbana, 1990) that prove to be useful in quantum well heterostructure devices. The "wet" oxidation process results in the conversion of high Al composition heterostructure material into a stable low refractive index, current-blocking native oxide that can be used to define optical cavities and current paths. The oxidation can be used to passivate exposed Al-bearing surfaces. Its selective, anisotropic nature is also useful for the fabrication of both planar and non-planar devices, including buried-oxide heterostructures. The III-V native oxide has been used in the fabrication of single-stripe and stripe-array lasers, ring lasers, coupled-cavity lasers, edge-defined buried-oxide lasers, buried-oxide window lasers, buried-oxide vertical cavity lasers, deep-oxide waveguides, deep-oxide lasers, and high reliability LED's. Also, the native oxide of AlAs has been demonstrated in field effect transistor operation. The use of the III-V native oxide in various device applications has been pioneered in this project.				
14. SUBJECT TERMS Al-based native oxide, III-V native oxide, "Wet" oxidation, buried III-V oxide, oxide-defined III-V devices, oxide-defined lasers, lateral oxidation, oxide-sealed LEDs			15. NUMBER OF PAGES 14	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED			16. PRICE CODE	
18. SECURITY CLASSIFICATION UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

19960522 112

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## ABSTRACT

At atmospheric conditions high Al composition  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x \geq 0.7$ ) in  $\text{Al}_x\text{Ga}_{1-x}\text{As-GaAs}$  heterostructures is subject to failure via hydrolyzation. In contrast, "wet" oxidation at higher temperatures ( $\geq 400^\circ\text{C}$ ) produces stable AlGaAs native oxides (Urbana, 1990) that prove to be useful in quantum well heterostructure devices. The "wet" oxidation process results in the conversion of high Al composition heterostructure material into a stable low refractive index, current-blocking native oxide that can be used to define optical cavities and current paths. The oxidation can be used to passivate exposed Al-bearing surfaces. Its selective, anisotropic nature is also useful for the fabrication of both planar and non-planar devices, including buried-oxide heterostructures. The III-V native oxide has been used in the fabrication of single-stripe and stripe-array lasers, ring lasers, coupled-cavity lasers, edge-defined buried-oxide lasers, buried-oxide window lasers, buried-oxide vertical cavity lasers, deep-oxide waveguides, deep-oxide lasers, and high reliability LED's. Also, the native oxide of AlAs has been demonstrated in field effect transistor operation. The use of the III-V native oxide in various device applications has been pioneered in this project.

## I. INTRODUCTION

By studying ( $\sim 1980$  to  $1990$ ) the atmospheric hydrolyzation (the environmental failure!) of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs quantum well heterostructures (QWHs), which for higher compositions ( $x \geq 0.7$ ) and thicker  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers ( $\geq 0.1 \mu\text{m}$ ) is a serious problem,<sup>1,2</sup> we have established that at still higher temperatures ( $\geq 400^\circ\text{C}$ ) and higher humidities (e.g.,  $\text{H}_2\text{O}$  vapor +  $\text{N}_2$ ) a useful stable Al-bearing native oxide of AlGaAs is formed.<sup>3,4</sup> Because of a phase change of Al-based compounds (e.g., AlAs) at higher temperature ( $\sim 400^\circ\text{C}$ ), the serious problem of destructive hydrolyzation is transformed into crystal oxidation. The stable Al-bearing III-V native oxide that is formed, which is insulating and has a relatively low index of refraction ( $n \sim 1.5$ ), proves to be useful in a number of devices. The Al-based native oxide has served, moreover, as the basis of a number of process and device patents. Besides seven issued patents (Refs. 4-10) (some with Hewlett-Packard) and several more that are due to issue, in the last 5 years we have generated an extensive set of journal publications (Refs. 11-55) on all aspects of the III-V native oxide and its use. All of this work on the III-V native oxide is listed here as Refs. 1 to 55. We note that this area of work, i.e., the Al-based III-V native oxide, originated in Urbana in this project.

We have established quite generally that, besides  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , a number of other III-V materials (heterolayers) with a significant Al composition (fraction) are candidates for "wet" oxidation.<sup>31,41,43</sup> This is particularly valuable for Al-based III-V heterosystems, including QWHs and superlattices, that are grown lattice matched, or nearly lattice matched, on GaAs substrates. These systems are automatically suitable (lattice matched) for incorporation of AlAs or high composition  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x \geq 0.7$ ) layers that then can be selectively "wet" oxidized, for example, as demonstrated in Ref. 52 or even earlier in Refs. 3, 33, 36, 38, 42, 44, and 46. The oxidized layer, which can be rendered in various geometrical forms, is useful for electrical and optical confinement, i.e., to define current paths and geometries as well as to define electromagnetic field distributions (cavity and mode configurations). The III-V native oxide expands considerably the technology and capability of optoelectronics, and like all new developments raises various problems for further study. In fact, the Al-based III-V native oxide that has originated in this work is now the subject of investigation and use in dozens of laboratories worldwide.

## II. NATIVE-OXIDE-DEFINED QUANTUM WELL LASERS

Since the first report of quantum well heterostructure diode lasers (p-n diode InP-InGaAsP QWHs grown by LPE; Rezek and Holonyak, Appl. Phys. Lett. **31**, 288 (1977) and Appl. Phys. Lett. **31**, 534 (1977)), many forms of stripe geometry QWH lasers have been reported. Perhaps the simplest have now been rendered via the use of the native oxide employed on the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs system.<sup>11,12,13,15,19,27,31,32</sup> We have not been limited, however, to only the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ -GaAs system and have employed the native oxide to define QWH lasers in also the following systems: (1) the strained layer system  $\text{Al}_y\text{Ga}_{1-y}\text{As}$ -GaAs- $\text{In}_x\text{Ga}_{1-x}\text{As}$ ,<sup>16,23</sup> (2) the visible-spectrum system  $\text{In}_{0.5}(\text{Al}_x\text{Ga}_{1-x})_{0.5}\text{P}$ - $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$ ,<sup>17,24,29,31</sup> and (3) the longer wavelength system InAlAs-InP-InGaAsP, the last for use at  $\lambda \sim 1.5 \mu\text{m}$ <sup>8,41</sup> or at  $\lambda \sim 1.3 \mu\text{m}$ <sup>43</sup> for low-loss fiber transmission. The broad scope of this work has made it apparent that the key component that, on the one hand, leads to atmospheric hydrolyzation and, on the other hand, supports oxidation at higher temperature (across a phase change) is a significant percentage of Al in the heterolayers.

Not only does the Al-based native oxide introduce simplification in the fabrication of single stripe and multiple stripe lasers, it also makes possible simplified fabrication of various forms of laser arrays,<sup>6,20,28,30</sup> not to mention various forms of ring lasers.<sup>5,25,39,51</sup> Stripe and ring geometries in active structures (lasers) make it evident that the native oxide technology provides the basis also for a new generation of passive waveguide structures.<sup>40,47</sup> In fact, by employing impurity induced layer disordering (IILD) to increase the Al composition at deeper depths,<sup>54</sup> i.e., down into the core active region of a QWH where oxidation problems are encountered,<sup>26,34</sup> we are able to use deep oxidation for large lateral refractive index changes that support unusually sharp bends in planar waveguide structures, in passive<sup>47</sup> or active structures.<sup>51</sup>

## III. LATERAL OXIDATION AND BURIED OXIDE LAYERS

From the inception of the Al-bearing III-V native oxide and its device use<sup>3,4</sup> we have appreciated that for higher Al concentrations, or for thicker  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  layers, "wet" oxidation proceeds "faster" laterally along a heterolayer than it does at lower compositions (smaller x) or for thinner layers. This is of special importance, because buried oxide devices can be constructed

employing anisotropic lateral oxidation, which is controlled by crystal composition and layer thickness.<sup>33,36,38,42,44,46,52</sup> We note that the lateral oxidation (buried oxidation) is effected via a crystal edge, mesa edge, an access well (an etched hole), a "trench," etc. This is unlike any other semiconductor oxide technology. It is a powerful new technology that offers special capabilities and devices. For example, buried oxides can be employed for high contrast Bragg mirrors in vertical cavity structures.<sup>33,36,44,46,49,52</sup> Also the oxide can be used to create buried apertures to control the current flow in a device, e.g., to prevent current flow near the failure-prone cleaved mirrors of a conventional stripe laser<sup>42</sup> or to define from above, and below, the active region of a laser.<sup>38</sup> In the case of the latter, the buried native oxide aperture defines the current flow, and thus excited region, in precisely the region defined simultaneously as the cavity. The precise overlap of the excited region and the cavity<sup>38</sup> is of special value in a vertical cavity surface emitting laser (VCSEL); VCSEL researchers have now discovered this (the importance of the results of Ref. 38) and have had cause to employ the oxide in redesigning the VCSEL with buried native-oxide current-defining collars. This is a revolutionary development in VCSELs and is based on the Urbana "wet" oxide technology of this project, e.g., Refs. 3, 4, 33 and 38.

#### IV. OXIDE DEVICE PASSIVATION AND RELIABILITY

An interesting aspect of the problem of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x \geq 0.7$ ) hydrolyzation, and thus the inevitable environmental decay of certain classes of devices, is that the basis exists, the Al itself, for higher temperature ( $\geq 400^\circ\text{C}$ ) "wet" oxidation and thus native oxide passivation of devices employing  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>14</sup> It is even possible to "wet" oxidize completed devices (metallized devices!), as in Ref. 42, and improve their reliability as we have recently reported (work with Hewlett-Packard).<sup>50</sup> Anywhere an edge, a mesa, a pit, a crevice exists that exposes an Al-bearing layer, the "wet" oxidation process can be employed to convert crystal to native oxide, and thus seal the structure. Since the native oxide is insulating, current is shunted away from oxidized regions, and any damage sealed by the oxide ceases to be current driven (hence is passive and more stable). We note that sooner or later VCSEL researchers, who in fact employ thick stacks of AlAs-GaAs heterolayers for Bragg mirrors, are apt to realize that their devices will suffer hydrolyzation unless

they are sealed. This is possible via the "wet" oxide.<sup>50</sup> The Al that hydrolyzes can be oxidized; instability can be converted into stability. This is an important discovery of this project.

## V. III-V NATIVE OXIDE INTERFACE PROPERTIES

The Al-bearing III-V native oxide technology we have introduced (Refs. 1-55), even in its present early state, is already important in optoelectronics (lasers, VCSELs, waveguides, etc.), not to mention for the improvement of device reliability (H-P LEDs, Ref. 50). Clearly this oxide technology is not nearly as "simple" as the 40+ year old  $\text{SiO}_2$ -on-Si technology that is at the heart of the IC industry. More complicated III-V materials are at issue. In addition, there is a large asymmetry in the electron and hole conductivity in III-V semiconductors, and it may never be possible to devise, for example, a III-V field effect transistor based on hole conduction that is equal to that based on electron conduction. Nevertheless, it makes sense to think that the Al-based III-V native oxide and its crystal interface will permit some forms of field effect transistors (FETs) to be realized. In fact, we show in Ref. 48 a first oxide-based FET; lateral oxidation (a natural form of "capped" oxidation) is used to form the buried native oxide that indeed supports the field effect operation. It is an open question concerning what further forms of FET's are possible employing the "wet" oxide process. Nevertheless, we have shown that the Al-based III-V native oxide will support a field (voltage), which means much more III-V MOSFET work will follow.

We note that the "wet" oxidation ( $\text{H}_2\text{O}$  vapor +  $\text{N}_2$ ,  $\geq 400^\circ\text{C}$ ) of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  does not yield a simple III-V native oxide, nor therefore a simple oxide-semiconductor interface. If  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is oxidized and then annealed sufficiently,  $\text{AlO}(\text{OH})$  is driven in the direction of  $\text{Al}_2\text{O}_3$ .<sup>37</sup> The former is more typical, and the latter less so because of processing limitations, i.e., the desire to employ moderate instead of high processing (annealing) temperatures. There is also a problem with the possibility of hydration. Thus, we do not consider it, nor is it, a simple matter to make a III-V native oxide FET.<sup>48</sup> Fortunately, in many applications, particularly in many forms of lasers, we are not dealing with an oxide-semiconductor interface in or near the active region, and the native oxide technology is more than adequate, even ideal, for certain purposes.

## VI. CONCLUSIONS

In a relatively short period coming after a long period (~1980 to 1990) of tracking and studying the destructive hydrolyzation of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $x \geq 0.7$ ), we have converted  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , as well as other Al-bearing III-V's, to a stable III-V native oxide useful in device technology. Besides the success of this work, which has yielded the patents and journal articles listed here as Refs. 1-55, ten doctoral students (see below) have completed work and theses in this new area of work since 1990 and have helped carry the III-V "wet" oxide technology to industry. In spite of its complicated form and early state of development, the III-V native oxide has already found its way into industrial use. Its use is spreading and its importance is growing. The Al-based III-V native oxide has changed optoelectronics fundamentally.

## VII. CONTRIBUTORS

As we have already mentioned, the III-V native oxide technology we introduced in 1990 has, besides its successful application in QWH lasers, yielded patents, papers, and 10 Ph.D. graduates who have carried the "wet" oxide technology to industry. These individuals are:

1. J. M. Dallesasse (1990, Phoenix Photonix)
2. F. A. Kish (1992, Hewlett-Packard)
3. A. R. Sugg (1993, Phoenix Photonix)
4. J. Caracci (1993, Wright-Patterson AFB)
5. T. A. Richard (1994, SDL)
6. N. A. El-Zein (1995, Motorola)
7. M. R. Krames (1995, Hewlett-Packard)
8. S. A. Maranowski (1995, Hewlett-Packard)
9. E. I. Chen (1996, Hewlett-Packard)
10. M.J. Ries (1996, MEMC)



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